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PATENT SPECIFICATION

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(54) INTUMESCENT SHEET MATERIAL

(71) We, MINNESOTA MINING AND MANUFACTURING COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 3M Center, Saint Paul, Minnesota 55101, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to flexible intumescent sheet material which is thermally resistant and is resilient after expansion. The invention further relates to the use of the flexible intumescent sheet material as a packing in positioning catalyst supports within containers.

It has become recognized that catalytic devices are needed for (1) oxidation of carbon monoxide and hydrocarbons and (2) reduction of the oxides of nitrogen in automobile exhaust gases in order to control pollution. Due to the relatively high temperatures encountered in these catalyzed processes, ceramic has been the natural choice for catalyst supports. Particularly useful supports are provided by ceramic honeycomb structures as described, for example, in U.S. RE 27,747.

Ceramic bodies tend to be frangible and to have coefficients of thermal expansion differing markedly from those of metal containers. Thus, the mounting of the ceramic body in the container must provide resistance to mechanical shock due to impact and vibration and to thermal shock due to thermal cycling. Both thermal and mechanical shock may cause deterioration of the ceramic support which, once started, quickly accelerates and ultimately renders the device useless. One material which has been found useful as a packing material for these purposes is a composition of 30—85% intumescent material, 0—60% inorganic fibrous material, 10 to 70% inorganic binder and optionally small amounts of organic binders, as described in parent Specification No: 1,476,183.

We find that this material has some disadvantages in application in that it tends to be rather stiff. This makes it difficult to roll the sheet material into supply rolls of small diameter.

It is an aim of this invention to produce a flexible intumescent sheet material and particularly an intumescent sheet material which can be rolled around an arc with radius of 5 cm. or less without cracking when at least about 2.5 mm. thick. It has been found that a sheet material may be produced from unexpanded vermiculite, inorganic fibrous materials and organic binders.

The present invention provides a flexible intumescent sheet material comprising from 30% to 75% by weight of expandable mica (as herein defined), from 20% to 65% by weight of inorganic fibrous material and from 5% to 20% of organic binder, the sheet material having a bulk density when dry of at least 0.5 g/ml. As used herein, the term "expandable mica" means any mica which swells upon heating but which is not exfoliated prior thereto. The sheet material can be made to a thickness of from 0.5 to 5 mm. by paper making techniques as will be described more fully hereinbelow.

Organic binders which may be used include various polymers and elastomers in latex form, for example, natural rubber latices, styrene-butadiene latices,

butadiene-acrylonitrile latices, latices of acrylate and methacrylate polymers and copolymers and the like. Elastomeric binders are preferred.

The invention also provides a process for the mounting of a ceramic structure in a metallic container including the step of providing at least one thickness of an intumescent sheet material according to the invention, between the ceramic structure and the container.

The flexible intumescent sheet material is particularly useful in automobile exhaust catalytic converters as a mounting material by expansion in situ. The expanded sheet then holds the ceramic core or catalyst support in place in the container or canister. The thermal stability and resilience of the sheet after exfoliation compensate for the difference in thermal expansion of the metal canister and the ceramic substrate, for vibration transmitted to the fragile device and for irregularities in the metallic or ceramic surfaces.

The sheet material may be formed by standard paper making techniques, either hand laid or machine laid, taking suitable precautions to attain substantially uniform distribution of particles throughout the web. The sheet material may be provided with or temporarily laminated to a backing sheet of kraft paper, plastics film, or a non-woven synthetic fiber web as desired. From 30 to 75% by weight of intumescent material, unexpanded beneficiated flakes of vermiculite ore in particle sizes of from 0.1 to 6 mm, preferably up to 2 mm., may be combined in a large volume of water with solids in the proportions 20 to 65% inorganic fibrous material, such as asbestos, e.g. chrysotile or amphibole asbestos, soft glass fibers such as available under the tradename chopped E. glass fiber, refractory filaments including zirconia-silica fibers, crystalline alumina whiskers and alumino-silicate fibers (available commercially under the tradenames Fiberfrax, Cerafiber and Kaowool) and 5 to 20% of elastomer as described above (the words "Fiberfrax" and "Kaowool" are registered Trade Marks). Small amounts of surfactants, foaming agents and flocculating agents may also be added before forming the sheet.

Flocculation is conveniently achieved using electrolytes such as alum, alkali or acid. Small amounts of organic fibrous materials may be added to impart additional green strength to the green sheet material. The intumescent material, inorganic fibrous material and organic binder may be blended together in a large volume of water, of the order of 5 to 100 times as much by weight and the flocculating agent or agents added. A small amount of surfactant or foaming agent may also be employed in order to improve the dispersion of the intumescent material without going beyond the scope of the invention. In order to avoid the use of asbestos in making the sheet, because of possible health hazards associated with this material, substitution of glass fiber materials or refractory (glass or crystalline) filaments or whiskers is possible without impairing the quality of the sheet. In general, asbestos fibers are less expensive than other fibers.

The sheet is conveniently formed by standard paper making techniques either on a hand-sheet former or Fourdrinier screen. The resulting green sheet is compressed to give a dry weight density of about 0.5 g./ml., or more, and dried at about 90°C. to form a handleable, readily flexible, resilient, intumescent sheet material. A strip of the material about 2.5 mm. thick can be curved to a radius of 5 cm. without cracking. Intumescent sheet materials of the invention are expanded at temperatures up to 500° to 800°C.

Measurement of the usefulness of the intumescent sheet material of the invention involves estimate of its ability to expand and to generate and maintain sufficient force against casing and substrate so as to hold catalyzed ceramic substrates in metal containers and yet absorb mechanical shock and to accommodate the differential dimensional changes resulting from thermal gradients. The method employed is summarized by the following procedure:

A preweighed 7.5 cm. diameter sample of intumescent sheet material is placed between fused silica platens, assembled within a furnace mounted on the frame of a suitable testing machine, such as an Instron ("Instron" is a registered Trade Mark). The cross-head of the testing machine is then adjusted so that the spacing between the fused silica platens is 3.56 ± .03 mm. The corresponding force in (Newtons) is noted and designated as "preload force". The furnace is then heated to 625°C. at a rate of about 300° C./hr. and the force generated is monitored on a strip chart recorder. The maximum force generated at 625°C. is noted. After allowing 20 minutes for furnace temperature and force stabilization, usually with a gradual decline from maximum force, the spacing between the platens is varied between 3.56 ± .03 mm. and 3.05 ± .03 mm. for 120 times over

about 10 min. These represent approximately maximum difference in dimensions due to temperature differences normally encountered between a substrate of 11.8 cm. diameter in a casing of 12.4 cm. inside diameter. The residual forces at the two spacings are noted initially and on the final cycle and are designated as "hot residual forces." The furnace is then cooled to 100°C. or lower and the spacing between platens is again varied 120 times between 3.56 and 3.05 mm. over about 10 min., the residual forces are again noted and are designated as "cold residual forces." The tested sample is then removed and reweighed to determine the weight of the thermally stable inorganic constituents. This weight is used to calculate the inorganic bulk density for the 3.05 mm. spacing. These densities usually are in the range of 0.4 to 1.1. The above-noted forces in Newtons are divided by the area of the sample, 45.58 cm.^{2}, and converted to pressures in Newtons/cm.^{2}. The most significant values are the maximum pressure at 625°C., the hot residual pressure at 625°C. and 3.56 mm. spacing and the cold residual pressure at 3.05 mm. spacing.

Preload pressures of up to 17 Newtons/cm.^{2} are typical depending upon the composition and density of the sample employed. Maximum pressures are rarely in excess of 100 Newtons/cm.^{2}.

Hot and cold residual pressures range from 3.5 to 35 and 0.7 to 14 Newtons/cm.^{2}, respectively, again depending on the composition and mass. In general, the greater the concentration of the intumescent material and the greater the sample density, the greater the pressures generated.

In employing an intumescent packing material with ceramic structures and particularly the present intumescent sheet materials, it is important to note that the force exerted against an unyieldable container during exfoliation of the intumescent sheet may be great enough to crush the ceramic substrate. Therefore, the thickness, density, mass and resilience of the mat, its expandability and the gap between the ceramic substrate and the container must be considered in designing and applying the intumescent sheet material.

The mounting material of the invention is also tested using a "hot-shake" test which is an extremely severe accelerated test. This test is performed on a catalyst canister assembly using an exhaust gas simulator, which simulates thermal conditions of exhaust gases from an engine and with the assembly coupled to a vibrator which simulates the extreme vibration of automotive conditions. Failure of a mounting system is determined by measuring the time required to displace a core from the canister by about 3 mm. The displacement occurs as a result of mounting material failures produced by thermal shock, mechanical shock, or a combination of both. No data are available correlating the total hours on the "hot-shake" test equipment to miles of normal or test driving.

A test catalytic canister assembly is simultaneously tested for mechanical and thermal shock resistance by attaching the catalytic converter assembly to a Maremont Exhaust Gas Simulator, Model EGS—3, and a L.A.B. Vibrator, Model RV—16—50, available from L.A.B. Corp., Scaneateles, New York. The exhaust gas simulator is set to produce about 28 ± 2.8 g./sec. of propane exhaust gas at 732 ± 28°C. measured at the catalytic converter inlet. The Vibrator produces a converter movement of about 5 mm. at 75 Hz. This provides acceleration of about 60 times that of gravity. Failure of the mounting is defined as time required to displace the core about 3 mm. An assembly made using the mounting material of the invention assembled as described above will usually not fail within 15 hours, i.e., 900 minutes. Survival for that time is usually considered adequate as most such assemblies will then also survive for much longer times, up to 100 hours.

Having described the invention in general terms, it is now more specifically illustrated by examples.

The following examples will more fully illustrate the best mode contemplated of practicing the invention.

EXAMPLE 1.

Water (1200 ml.) is poured into the mixing chamber of a large Waring Blendor and to it is added 13.34 g. of glass fiber (washed Fiberfrax available from the Carborundum Company) followed by vigorous agitation for about 20 seconds. Then there is added 6.67 g. of styrene-butadiene as 16.68 g. of 40% latex (available as Hycar 1562 x 103 from B. F. Goodrich Chemical Co.) followed by agitation for 10 seconds, the addition of 46.7 g. unexpanded vermiculite ore (No. 3 grade Zonolite, about 0.4 to 1.7 mm. diameter from W. R. Grace and Co.) and further agitation for about 15 seconds (the words "Hycar" and "Zonolite" are registered Trade Marks). The latex is flocculated and at least partially deposited on the fibers

by adding a small amount of 10% alum solution (sufficient to reduce the pH to a range of 4.5 to 5) to the slurry and mixing for about 10 seconds. The suspension is cast onto a hand former to give a hand sheet of about 19 x 20 cm., total area about 380 cm.², which is dried. The dry sheet is too low in density and an important step is to densify it. The sheet is compressed between platens to about 2.2 mm. thickness to give a density of about 0.8 g./ml. It is flexible and can be rolled around a radius of 5 cm.

Strips of this prepared sheet are placed in the space between an about 11.8 cm. diameter cylindrical catalyst-impregnated ceramic substrate and an about 12.4 diameter cylindrical container. The assembly is heated to 625°C. from room temperature at a rate of 300°C./hr. to exfoliate the green sheet, resulting in a securely mounted ceramic core within the container.

EXAMPLE 2.

An intumescent sheet of the invention is prepared as described above in Example 1 using 2400 ml. of water, 22.14 g. glass fiber, 5.80 g. of styrene-butadiene (14.50 g. of 40% latex), and 77.47 g. of unexpanded vermiculite ore. It is cast as a sheet and compressed to about 3.5 mm. thickness. It can be rolled around a curve of radius 5 cm. without cracking portion of the sheet of about 45.58 cm.² (weighing 12.76 grams) is placed between fused silica plating and tested as described above. It is first heated to 625°C. at 300°C./hr., and found to generate a maximum pressure of about 75 Newtons/cm.² and thereafter to give hot and cold residual pressures in Newtons/cm.² as indicated in Table 1.

TABLE 1

Spacing	Residual	Pressure at 625°C.	Residual	Pressure at 25°C.
	Initial	after 120 cycles	Initial	after 120 cycles
3.56 mm.	74.6	49.7	14.8	10.8
3.05 mm.	16.1	3.3	0	0

Strips of the sheet material are placed in the spaces between an about 11.8 cm. diameter catalyst impregnated ceramic substrate and a mild steel cylindrical container of about 12.4 cm. inside diameter as described in Example 1 and heated to 625°C. from room temperature at a rate of about 300°C./HR. to exfoliate the intumescent sheet. The ceramic substrate is found to be securely mounted within the metal container. Such ring flanges and end cones are subsequently welded to the metal container to produce a complete catalytic converter assembly.

EXAMPLE 3.

Using the same procedures and forming techniques as in Example 1, intumescent sheets of varying thicknesses compressed to different densities are made using 7.5% Hycar 1562X103 binder, 30% Fiberfrax glass fiber and 62.5% No. 4 unexpanded vermiculite ore. These resulting intumescent sheet materials are used to mount catalyst impregnated ceramic substrates in complete catalytic converter assemblies as described in Example 1. The amounts of mounting material provide inorganic residues at 3.05 mm. thickness, herein referred to as "end use densities", ranging from .32 g./ml. to 1.12 g./ml. The converters are then subjected to "hot shake" testing. The converter in which there was an end use density of 0.32 g./ml. failed in 15 min., the others of 0.48, 0.64, 0.80, 0.96 and 1.12 g./ml. survived for 900 minutes when the tests were terminated.

Portions of sheet materials of end use density of 0.48, 0.64 and 0.80 are also characterized as to pressure generation as described above. These showed maximum pressures of 10.5, 22.4 and 63 Newtons/cm.², respectively. These are tabulated in Newtons/cm.² in Table 2.

TABLE 2

Sample end use density g./ml.	Spacing	Residual	Pressure at 625°C.	Residual	Pressure at 25°C.
		Initial	after 120 cycles	Initial	after 120 cycles
0.48	3.56	4.3	1.7	0	0
048	3.05	24.1	20.6	0.3	0.1
0.64	3.56	14.5	10.4	0	0
0.64	3.05	52.6	47.6	1.8	1.3
0.80	3.56	35.7	26.7	0.2	0.1
0.80	3.05	98.1	9.0	13.8	9.6

EXAMPLE 4.

Using the same batching and forming techniques, as in Example 1, an intumescent sheet of 2.1 mm. thickness and bulk density of .80 g./cc. is made using the procedures of Example 1 to contain 12% styrene-butadiene binder, 35% glass fiber, and 53% No. 4 unexpanded vermiculite ore (size range .1 mm. to .6 mm. in diameter). This material is then used to fabricate a complete catalytic converter assembly as also described in Example 1. It is subjected to the "hot shake" test as described above and readily survives for 900 minutes. Similarly prepared catalytic converters in which the mounting material is an Inconel X—750 wire mesh, vermiculite ore, expanded vermiculite or a sheet of glass fiber and latex without vermiculite fail to survive for 900 minutes ("Inconel" is a registered Trade Mark). The converter employing wire mesh survives for 415 minutes, the others all less than 45 minutes. In each case, except for the wire mesh, the same end-use bulk density of mounting material of 0.48 g./ml. is attained.

EXAMPLE 5.

The intumescent sheet materials of Examples 1 to 4 are provided with backing sheets of nonwoven webs of synthetic fiber or kraft paper and wound into rolls. It is found that the rolls are readily unwound without tendency for sticking between consecutive convolutions.

WHAT WE CLAIM IS:—

1. A flexible intumescent sheet material comprising from 30% to 75% by weight of expandable mica (as herein defined), from 20% to 65% by weight of inorganic fibrous material, and from 5% to 20% of organic binder, the sheet material having a bulk density when dry of at least 0.5 g./ml.

2. An intumescent sheet material according to Claim 1 in which the expandable mica is vermiculite.

3. An intumescent sheet material according to Claim 1 or Claim 2 in which the inorganic fibrous material is one of asbestos, soft glass fibre, and refractory alumino-silicate fibre.

4. A intumescent sheet material according to any preceding Claim additionally having a backing sheet of one of kraft paper, plastics film, and nonwoven synthetic fibre web.

5. An intumescent sheet material according to any preceding Claim wherein the organic binder is elastomeric.

6. A flexible intumescent material according to Claim 1 and substantially as herein described.

7. A process for the mounting of a ceramic structure in a metallic container including the step of providing at least one thickness of an intumescent sheet material according to any preceding Claim between the ceramic structure and the container.

8. A process according to Claim 7 wherein said at least one thickness is 0.5 to 5 mm. thick.

9. A process for the mounting of a ceramic structure in a metallic container according to Claim 5 and substantially as herein described.

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